Journal of the

OPTICAL SOCIETY

of AMERICA

Rotational and Vibrational Constants of the HCl^{35} and DCl^{35} Molecules*

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(Received May 25, 1961)

The 1–0, 2–0, 3–0, 4–0, and 5–0 bands of HCl^{35} and the 1–0 and 2–0 bands of DCl^{35} have been measured with high precision. A critical analysis has been made to determine the rotational and vibrational constants of these molecules. It is necessary to use a polynomial in m of the sixth degree to satisfactorily represent the frequencies of the band lines in the case of the most precisely measured bands. B_0 for HCl^{35} has been found to have a value of 10.440254±0.000010 cm^{-1}. B_0 for DCl^{35} was found to be 5.392261 ±0.000010 cm^{-1}. When the B_0 obtained for DCl^{35} is combined with the microwave measurement of B_0 by Cowan and Gordy the value obtained for the velocity of light $c = 299 793.1 ±0.65$ km/sec. The observed rotational and vibrational constants (Y_{lj}) have been used to calculate the potential constants of HCl^{35} by

making use of Dunham's theory of a rotating vibrator. It is shown that HCl^{35} is not a pure rotating vibrator since the observed and calculated values of $Y_{02} \sim D_e$ are in disagreement by about 1 part in 1000 which is approximately 10 times the experimental error. By making use of the molecular constants for HCl^{35} and DCl^{35} and the accurately known atomic masses it is deduced that the ground level B_e is perturbed by the upper electronic levels by 1 part in 8000. The sign of the perturbation is to increase B_e over its unperturbed value. The sign of the perturbation is such that it may be presumed the HCl molecule has a positive magnetic moment. It was calculated that $\mu_J = +0.2$ and $+0.1$ nuclear magnetons, respectively, for HCl^{35} and DCl^{35}.

INTRODUCTION

A VERY general potential function has been used by Dunham[1] to derive the energy levels of a rotating vibrator. He has carried the computation to a sufficiently high degree of approximation so that the various coefficients of the powers of $(v+\frac{1}{2})$ and $J(J+1)$ in the energy level formulas are really a series in powers of the ratio B_e^2/ω_e^2. Thus the familiar observable band-spectrum constants B, D, etc., ω, $x\omega$, etc. must be replaced by quantities Y_{lj}, where l and j refer to the power of $(v+\frac{1}{2})$ and $J(J+1)$ associated with the particular Y.

The difference between the Dunham approximation and the usual approximation due to Fues[2] is small and completely negligible except for very light molecules, and even then, the experimental data must be of the highest accuracy to detect the presence of the correction terms. Dunham's theory applies strictly only to a pure rotating vibrator. He has proposed a test to determine if the real molecule is a pure rotating vibrator, namely, that the observed value of $Y_{02} \sim D_e$ is the value calculated from the theory. It is to be expected that the

motion of the electrons may cause perturbations which make the real molecule deviate slightly from a pure rotating vibrator.

Rosenblum *et al.*,[3] in their investigation of the isotopic mass ratios in the molecule CO by the most refined and precise methods of microwave spectroscopy, have shown that even in the case $v=0$, it is necessary to take account of electronic perturbation of the rotational energy levels.

The subject of the present investigation is the molecule HCl^{35} and the isotopic molecule DCl^{35}. We have previously reported precision measurements[4] on the 1–0, 2–0, 3–0, 4–0, and 5–0 bands of HCl^{35} and the 2–0 band of DCl^{35}. Recent improvements in the "Echelle" spectrograph[5] and the addition of a large number of new absorption wavelength standards have allowed us to refine some of the previous measurements, and ·make the measurements on one of the bands more complete (1–0 band of HCl^{35}). Recently Plyler and, Tidwell[6] have measured the 1–0 bands of HCl^{35} and HCl^{37}. In addition we have now made measurements on the 1–0 band of

[3] B. Rosenblum, A. H. Nethercot, and C. H. Townes, Phys. Rev. 109, 400 (1958).
[4] D. H. Rank, W. B. Birtley, D. P. Eastman, B. S. Rao, and T. A. Wiggins, J. Opt. Soc. Am. 50, 1275 (1960).
[5] D. H. Rank, D. P. Eastman, W. B. Birtley, G. Skorinko, and T. A. Wiggins, J. Opt. Soc. Am. 50, 821 (1960).
[6] E. K. Plyler and E. D. Tidwell, Z. Electrochem. 64, 717 (1960).

[1] J. L. Dunham, Phys. Rev. 41, 721 (1932).
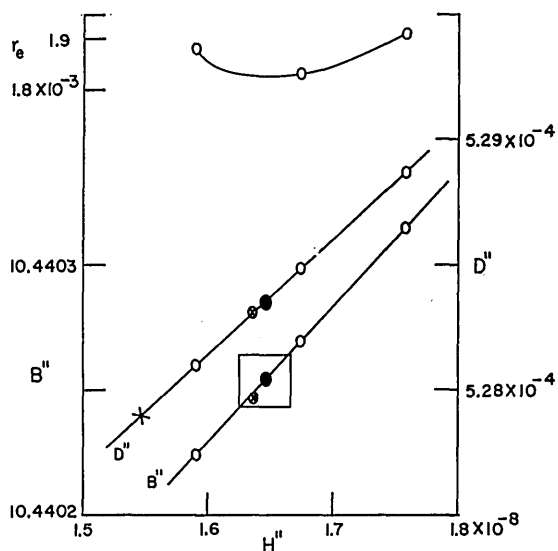[2] E. Fues, Ann. Physik 80, 367 (1932).

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FIG. 1. Plot of B'', D'', and r_e for various values of H''. The open circles are values obtained in fixing H'' and solving for B'' and D'' by least squares. The ⊗ circles are the values obtained by a three-variable least-squares solution. The solid circles represent the graphical solution of B'' and D''. The box represents the possible variation in H'' for an error in B'' of 1 part in 10^6. The × point is the D expected from Dunham's theory.

DCl³⁵. A full description of the experimental modifications etc., will appear in the *Journal of the Optical Society of America* in the near future. The experimental situation with regard to these spectra is now sufficiently precise and complete so that a critical analysis can now be made at the level of the Dunham approximation.

We shall follow Dunham[1] in defining energy levels in the following form

$$F_{v,J} = \sum_{lj} Y_{lj}(v+\tfrac{1}{2})^l J^i (J+1)^j. \qquad (1)$$

The above expression differs from the usually used convention in that the laws of algebra determine the algebraic sign of the Y's while in the conventional formulas, $x\omega$, α, and D are arbitrarily given positive signs and the $F_{v,J}$ function adjusted to make these inherently negative quantities come out positive.

The lower- and upper-state rotational constants for the various bands have been determined from the following combination relationships:

$$\Delta_2 F'' = (4B'' + 6D'' + 27/4H'')(J+\tfrac{1}{2}) + (8D'' + 34H'')(J+\tfrac{1}{2})^3 + 12H''(J+\tfrac{1}{2})^5 \qquad (2)$$

$$R(J-1) + P(J) = 2\nu_0 + 2[(B'-B'') + (D'-D'')]J^2 + 2[(D'-D'') + 3(H'-H'')]J^4 + 2(H'-H'')J^6. \qquad (3)$$

The symbols involved have their usual band-spectroscopic significance.

GROUND STATE OF HCl³⁵

From the 30 $\Delta_2 F''$ values obtained from the 1–0 and 2–0 bands we have determined B'', D'', and H'' by the application of the least-squares method. The values obtained for the rotational constants were $B'' = 10.440247$, $D'' = -5.28308 \times 10^{-4}$, and $H'' = 1.6367 \times 10^{-8}$, all expressed in cm⁻¹. Equation (2) has 3 degrees of freedom. It is well known that the molecular constants are interrelated. The least-squares procedure does not take cognizance of the interrelationships (which are not known with sufficient exactness). Thus the imposed condition of arbitrariness of the constants may slightly distort the values obtained for these constants by means of the least-squares procedure. In addition it is somewhat doubtful if we have carried enough figures (10 place calculating machine) to do the mathematical curve-fitting process to minimize the residuals strictly.

We believe a somewhat more precise and realistic determination of B'', D'', and H'' was accomplished in the following manner. Three least-square calculations were made of the data by using three different values of H'' in the neighborhood of the H'' previously determined. The $\Delta_2 F''$ values were corrected for the assumed value of H'' and these corrected values treated to least squares. Thus the number of degrees of freedom in Eq. (2) as modified is reduced to 2. The result of these calculations is that three values of B'', D'', and H'' have been obtained as well as three sets of residuals.

The best values for B'', D'', and H'' will be those for which $r_e = [\sum (r^2/n\text{-}1)]^{\frac{1}{2}}$ is a minimum. We have determined B'', D'', and H'' from the curves shown in Fig. 1 where B'', D'', and r_e are plotted against H''. The values obtained by means of the graphical procedure were $B'' = 10.440254$, $D'' = -5.28350 \times 10^{-4}$, and $H'' = 1.6460 \times 10^{-8}$. In Fig. 1 we have indicated the graphical solution by means of the solid circles and the solution of Eq. (2) by means of the points indicated by the symbol ⊗. We have constructed a box around the graphical

TABLE I. Calculated and observed $\Delta_2 F''$'s obtained from the 1−0 and 2−0 bands of HCl³⁵.

$J+\tfrac{1}{2}$	$\Delta_2 F''$ Calc	2−0 Obs	×10⁻³ C−O	1−0 Obs	×10⁻³ C−O
1.5	62.6225	.6209	1.6	.6287	−6.2
2.5	104.3286	.3264	2.2	.3237	4.9
3.5	145.9714	.9706	0.8	.9753	−3.9
4.5	187.5256	.5273	−1.7	.5263	−0.7
5.5	228.9661	.9634	2.7	.9650	1.1
6.5	270.2677	.2706	−2.9	.2664	1.3
7.5	311.4057	.4014	4.3	.4046	1.1
8.5	352.3551	.3584	−3.3	.3542	0.9
9.5	393.0915	.0912	0.3	.0905	1.0
10.5	433.5903	.5940	−3.7	.5907	−0.4
11.5	473.8275	.8241	3.4	.8282	−0.7
12.5	513.7791	.7757	3.4	.7836	−4.5
13.5	553.4215	.4230	−1.5	.4217	−0.2
14.5	592.7313	.7288	2.5	.7302	1.1
15.5	631.6855	.6823	3.2		
16.5	670.2614	.2636	−2.2	.	

TABLE II. The rotation vibration constants and Dunham potential constants of HCl^{35}.
The dots indicate that the corresponding value was used in the fitting.

	B_v Obs	B_v Calc		Y_{lj} Experimental	Y_{lj} Dunham
B_0	10.440254	$\cdots$	$Y_{01} \sim B_e$	10.593404	(true $B_e = 10.593580$)
B_1	10.136223	$\cdots$	$Y_{11} \sim \alpha$	-0.307139_4	
B_2	9.834663	$\cdots$	$Y_{21} \sim \gamma$	1.7343×10^{-3}	
B_3	9.534909	$\cdots$	$Y_{31} \sim \delta$	-1.1083×10^{-4}	
B_4	9.2360	9.236630			
B_5	8.942	8.938161			
	D_v Obs$\times 10^{-4}$	D_v Calc$\times 10^{-4}$			
D_0	-5.28350	$\cdots$	$Y_{02} \sim D_e$	-5.32019×10^{-4}	-5.31563×10^{-4}
D_1	-5.21665	$\cdots$	$Y_{12} \sim B_e$	$+7.556 \times 10^{-6}$	$+7.18 \times 10^{-6}$
D_2	-5.15851	$\cdots$	$Y_{22} \sim \pi$	-4.355×10^{-7}	-2.12×10^{-7}
D_3	$\cdots$	-5.10908			
	H_v Obs$\times 10^{-8}$				
H_0	1.6460		$Y_{03} \sim H_e$	1.6674×10^{-8}	$+1.6953 \times 10^{-8}$
			$Y_{13} \sim \delta H_e$		-4.28×10^{-10}
			Y_{04}		$+1.07 \times 10^{-11}$
	ν_0 Obs	ν_0 Calc			
$1-0$	2885.9775	$\cdots$	$Y_{10} \sim \omega_e$	2990.97424	(true $\omega_e = 2991.0676$)
$2-0$	5667.9841	$\cdots$	$Y_{20} \sim x_e \omega_e$	-52.84579	
$3-0$	8346.782	$\cdots$	$Y_{30} \sim y_e \omega_e$	0.23445	
$4-0$	10 922.81	10 922.811	$Y_{40} \sim z_e \omega_e$	0.01343	
$5-0$	13 396.19	13 396.189			
				$a_1 = -2.364350$	
				$a_2 = +3.661987$	
				$a_3 = -4.710056$	
				$a_4 = +5.322654$	

solution point whose size indicates an error in B'' of 1 part in 10^6. The point marked by an X on the D'' vs H'' curve will be referred to in a later section of this paper. The fit of the $\Delta_2 F''$ values to the constants obtained graphically is given in Table I.

UPPER-STATE CONSTANTS

The 1–0 and 2–0 bands were analysed by the application of Eq. (3) by means of the least-squares method. After determination of all of the Y's the potential constants were computed from Dunham's equations. A value of Y_{13} was then computed from these potential constants. After obtaining Y_{13} Eq. (3) was corrected for the term in J^6 and B' and D' values redetermined from the data. In the case of the 3-0, 4-0, and 5-0 bands the previously determined $\Delta_2 F''$ values (calculated) were used to supplement the "band-origin" data whenever possible because of certain lines not having been measured. The constants Y_{12} and Y_{22} could be determined from the very precisely measured 1–0 and 2–0 bands, and were used to compute $D'-D''$ for the 3–0 band, thus only making it necessary to determine ν_0 and B' from the 3–0 band data.

We have summarized the determination of the rotational constants in Table II. In Tables III–V we have tabulated the observed frequencies and the calculated frequencies of the band lines for the 1–0, 2–0, and 3–0 bands, respectively. It is of course necessary to use a 6th-power equation to represent the frequencies of the band lines.

VIBRATIONAL CONSTANTS

We have fitted the observed band origins to an equation terminating with $(v+\frac{1}{2})^4$. The 1–0, 2–0, and 3–0 bands were fitted exactly. The 4–0 and 5–0 bands were both used to determine the fourth constant. However the result would have been essentially the same if either band had been used separately.

We have summarized the final determination of the molecular constants in Table II. We have also included the results of the application of Dunham's theory to the observed Y's. The potential constants a's are certainly not accurate to nearly the number of significant figures calculated. It is necessary however to carry the large number of figures to make the solutions of the complicated Dunham equations significant. We are indebted to Dr. A. H. Guenther of Kirtland Air Force Base, Albuquerque, New Mexico, for furnishing us with explicit expressions for Dunham's a's which made our computations much less laborious.

It can be seen from Table II that the observed and calculated values of Y_{02} differ by 1 part in 1000. This discrepancy we consider to be between 5 and 10 times the experimental error of the Y_{02} determination. Dunham has pointed out that if Y_{02} calculated and Y_{02} measured do not agree, the molecule is not a pure rotating vibrator. It can be seen by inspection of Fig. 1, D'' vs H'' curve that the D'' expected from Dunham's theory (which is the point indicated by an $\times$) is certainly not compatible with the experimental data. It seems certain that the ground state must be perturbed

TABLE III. Calculated and observed frequencies in vacuum wave numbers of the 1−0 band of HCl[35].[a]

J	$R(J)$ Calc	$R(J)$ Obs	$\times 10^{-3}$ C−O	Std	$P(J)$ Calc	$P(J)$ Obs	$\times 10^{-3}$ C−O	Std
0	2906.2479	.2521	−5.8	J				
1	25.8977	.8950	2.7	B	2865.0991	.0967	2.4	A
2	44.9146	.9154	−0.8	F	43.6254	.6234	2.0	A
3	63.2864	.2865	−0.1	F	21.5691	.5713	−2.2	A
4	81.0013	.0013	0.0	E	2798.9432	.9401	3.1	K
5	98.0473	.0438	3.5	A	75.7609	.7602	0.7	2−0
6	3014.4130	.4114	1.6	A	52.0353	.0363	−1.0	B
7	30.0870	.0862	0.8	B	27.7796	.7774	2.2	D
8	45.0583	.0569	1.4	A	03.0074	.0068	0.6	C
9	59.3160	.3179	−1.9	A	2677.7320	.7320	0.0	C
10	72.8495	.8490	0.5	2−0	51.9669	.9664	0.5	C
11	85.6485	.6539	−5.4	A	25.7258	.7272	−1.4	A
12	97.7029	.7034	−0.5	B	2599.0221	.0208	1.3	B
13	3109.0029	.0026	0.3	C	71.8695	.8703	−0.8	D
14	19.5392	.5362	3.0	A	44.2815	.2817	−0.2	B
15	29.3023	.2972	5.1	C	16.2718	.2724	−0.6	C

[a] $r_e = 1.59 \times 10^{-3}$.

by the upper electronic states in a significant amount. We shall return to this problem of perturbation of the ground level after we have treated the measurements on DCl[35].

DCl[35] BANDS

It was suggested by Kemble[7] that the relationships between the molecular constants of isotopic molecules can be written in the form

$$Y_{lj}{}^i / Y_{lj} = \rho^{(l+2i)}, \qquad (4)$$

where $\rho^2 = m/m^i$ and m, and m^i are, respectively, the reduced masses of the isotopic molecules. Dunham[1] has shown that these simple expressions require a slight modification to the form,

$$Y_{lj}{}^i / Y_{lj} = \rho^{(l+2i)}[1 + (\beta_{lj}/\alpha_{lj} \times B_e^2/\omega_e^2)(\rho^2 - 1)], \qquad (5)$$

and he has explicitly defined β_{lj} and α_{lj} in terms of the molecular potential constants. The correction terms are very small but certainly are significant when dealing with very precise measurements.

We have made measurements on the 1–0 and 2–0 bands of DCl[35]. It is immediately apparent that the constants D, β, H, $y_e\omega_e$, and $z_e\omega_e$ are very much smaller in DCl[35] than in HCl[35] since they involve high powers of ρ. We feel that we can compute these constants for DCl[35] from the HCl[35] measurements with considerably better accuracy than by measuring them directly. We have calculated ρ from the atomic masses given by Townes and Schawlow[8] and find $\rho = 0.7172031$.

The procedure employed in the analysis was to correct the $\Delta_2 F''$ values for the terms in $(J + \frac{1}{2})^3$ and $(J + \frac{1}{2})^5$ by means of constants calculated from the isotope relations. The first term in $(J + \frac{1}{2})$ was then determined

TABLE IV. Calculated and observed frequencies in vacuum wave numbers of the 2−0 band of HCl[35].[a]

J	$R(J)$ Calc	$R(J)$ Obs	$\times 10^{-3}$ C−O	Std	$P(J)$ Calc	$P(J)$ Obs	$\times 10^{-3}$ C−O	Std
0	5687.6514	.6498	1.6	A				
1	5706.0951	.0932	1.9	A	5647.1057	.1075	−1.8	A
2	23.3033	.3024	0.9	A	25.0289	.0289	0.0	B
3	39.2642	.2654	−1.2	A	01.7665	.7668	−0.3	B
4	53.9663	.9673	−1.0	A	5577.3319	.3318	0.1	A
5	67.3986	.3980	0.6	A and C	51.7386	.7381	0.5	B
6	79.5504	.5498	0.6	C	25.0003	.0039	−3.6	B
7	90.4113	.4147	−3.4	C and K	5497.1309	.1274	3.5	B
8	99.9713	.9688	2.5	B	68.1448	.1484	−3.6	B
9	5808.2208	.2205	0.3	B	38.0563	.0563	0.0	C
10	15.1505	.1481	2.4	B	06.8799	.8776	2.3	B
11	20.7516	.7520	−0.4	C	5374.6306	.6265	4.1	C
12	25.0156	.0180	−2.4	C	41.3231	.3240	−0.9	A
13	27.9345	.9320	2.5	$R(16)$	06.9727	.9763	−3.6	A
14	29.5004	.5006	−0.2	C	5271.5943	.5950	−0.7	A
15	29.7062	.7079	−1.7	C	35.2033	.2032	0.1	A
16	28.5450	.5420	3.0	C	5197.8151	.8183	−3.2	A
17					59.4450	.4443	0.7	A

[a] $r_e = 1.42 \times 10^{-3}$.

[7] R. S. Mulliken, Phys. Rev. **25**, 126 (1925).
[8] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955), p. 644.

TABLE V. Calculated and observed frequencies in vacuum wave numbers of the 3−0 band of HCl³⁵.[a]

J	$R(J)$ Calc	$R(J)$ Obs	×10⁻³ C−O	Std	$P(J)$ Calc	$P(J)$ Obs	×10⁻³ C−O	Std
0	8365.8494	.8442	5.2	C				
1	83.0943	.0841	10.2	C	8325.9032	.9078	−4.6	2−0
2	98.5044	.4987	5.7	C				
3	8412.0687	.0712	− 2.5	2−0	8278.7656	.7663	−0.7	C
4	23.7756	.7853	− 9.7	A	52.5331	.5349	−1.8	B
5	33.6147	.6247	−10.0	A	24.5430	.5436	−0.6	A
6	41.5771	.5718	5.3	A	8194.8097	.8068	2.9	A
7	47.6519	.6582	− 6.3	B	63.3475	.3479	−0.4	A
8	51.8306	.8322	− 1.6	A	30.1715	.1714	0.1	A
9	54.1045	.0995	5.0	B				
10	54.4655	.4634	2.1	B				

[a] $r_e = 3.65 \times 10^{-2}$.

by least squares by using only $\Delta_2 F''$ values in excess of 100 cm⁻¹. (The smaller $\Delta_2 F''$ values can only reduce the precision of the B'' determination since only one constant remains to be determined from the data.) The value obtained for B_0 was 5.392261 cm⁻¹ ±0.000010 cm⁻¹, D_0 calculated $= -1.40064 \times 10^{-4}$ cm⁻¹.

In Table VI we have given the measured and calculated values of the $\Delta_2 F'''$'s for DCl³⁵.

Cowan and Gordy[9] have measured the pure rotation transition $J \sim 0-1$ for DCl³⁵ and obtain 323 295.77±0.13 Mc/sec. When our accurate D_0 is used we obtain $B_0 = 161\ 656.28_3 \pm 0.075$ Mc/sec. If the microwave value is combined with the infrared measurement we obtain c (the velocity of light) $= 299\ 793.1 \pm 0.65$ km/sec, a value well within the present confidence limit of our knowledge of c. It seems appropriate to remark that we believe the B_0 value we have obtained for HCl³⁵ has several times the accuracy of the B_0 we have determined for DCl³⁵. Thus if microwave spectroscopists can measure B_0 for HCl³⁵ with sufficient exactness a c determination will be available with an accuracy equal to or greater than that determined by any other method up to the present time.

We have made use of the isotope relations in conjunction with Eq. (3) to compute the terms in J^4 and J^6. Thus we are able to determine $(B' - B'')$ and ν_0 from the band origin equation for the 1-0 and 2-0 bands. We have used B_0 and B_2 to determine Y_{11} and Y_{01} since Y_{21} and Y_{31} have been calculated from the isotope relations. Since B_1 has not been used to determine any of the constants it can be used as a check on our accuracy. We obtain B_1 (observed) $= 5.279816$ and B_1 (calculated) $= 5.279819$, an agreement which is eminently satisfactory. We have used ν_0 for the 1-0 and 2-0 bands to determine Y_{10} and Y_{20}. (Y_{30} and Y_{40} were calculated from the isotope relations.)

In Tables VII and VIII we have presented the observed and calculated frequencies of the band lines for the 1-0 and 2-0 bands of DCl³⁵.

Table IX contains a summary of the DCl³⁵ molecular constants and the Y's calculated from Dunham's

equations. The Y's marked with a superscript [a] were obtained from HCl³⁵ by making use of the isotope relationships.

PERTURBATION OF THE GROUND LEVEL

By making use of Eq. (5) we find

$$B_e{}^i/B_e \sim Y_{01}{}^i/Y_{01} = \rho_D{}^2 (1 + 0.0000086) = 0.5143573 \quad (6a)$$

and

$$\omega_e{}^i/\omega_e \sim Y_{10}{}^i/Y_{10} = \rho_D (1 + 0.0000152) = 0.7172121 \quad (6b)$$

We obtain $\rho_D{}^2 = 0.5143531 =$ true $B_e{}^i/$true B_e and from the ω_e relationship $\rho_D = 0.7172013 =$ true $\omega_e{}^i/$true ω_e. The ρ value obtained from ω_e is in satisfactory agreement with $\rho = 0.7172031$ as calculated from the atomic masses. The ρ value obtained from B_e is, however, not in agreement.

Mulliken and Christy[10] have theoretically treated the perturbations of the molecular B values by upper electronic states. For HCl there are two pure cases possible, the separate atom approximation, which gives rise to Van Vleck's condition of pure precession and the united atom approach which would give a zero result. Our case

TABLE VI. Calculated and observed $\Delta_2 F'''$'s obtained from the 1−0 and 2−0 bands of DCl³⁵.

$J+\frac{1}{2}$	$\Delta_2 F''$ Calc	2−0 Obs	×10⁻³ C−O	1−0 Obs	×10⁻³ C−O
1.5	32.3485	.3403	8.2		
2.5	53.9030	.9016	1.4		
3.5	75.4407	.4376	3.1	.4425	−1.8
4.5	96.9548	.9516	3.2	.9569	−2.1
5.5	118.4388	.4381	0.7	.4393	−0.5
6.5	139.8859	.8855	0.4		
7.5	161.2894	.2889	0.5	.2933	−3.9
8.5	182.6428	.6401	2.7		
9.5	203.9394	.9438	−4.4		
10.5	225.1725	.1727	−0.2		
11.5	246.3357	.3353	0.4		
12.5	267.4223				
13.5	288.4261				
14.5	309.3404	.3377	2.7		

[9] M. Cowan and W. Gordy, Phys. Rev. 111, 209 (1958).

[10] R. S. Mulliken and A. Christy, Phys. Rev. 38, 87 (1931).

TABLE VII. Calculated and observed frequencies in vacuum wave numbers of the 1−0 band of DCl[35].[a]

J	$R(J)$ Calc	$R(J)$ Obs	$\times 10^{-3}$ C−O	Std	$P(J)$ Calc	$P(J)$ Obs	$\times 10^{-3}$ C−O	Std
0	2101.6204	.6240	−3.6	F				
1	11.9512	.9513	−0.1	G	2080.2773	.2751	2.2	C
2	22.0506	.0508	−0.2	B	69.2719			
3	31.9152	.9159	−0.7	G	58.0482			
4	41.5418	.5398	2.0	D	46.6099	.6083	1.6	G
5	50.9272	.9279	−0.7	G	34.9603	.9590	1.3	2−0 DCl
6	60.0683	.0689	−0.6	B	23.1029	.1005	2.4	G
7	68.9619	.9632	−1.3	G	11.0412			
8	77.6050				1998.7788	.7756	3.2	G
9	85.9946				86.3190			
10	94.1277				73.6656			
11	2202.0014				60.8221			
12	09.6127	.6078	4.9	G	47.7920			
13	16.9589	.9614	−2.5	C	34.5789			
14	24.0371	.0370	0.1	C	21.1865			
15	30.8446	.8471	−2.5	G	07.6184			
16	37.3788	.3790	−0.2	C	1893.8782			

[a] $r_e = 1.43 \times 10^{-3}$.

with HCl will be intermediate between the above mentioned cases.

Professor Mulliken has pointed out (private communication with D. H. R.) that it can be presumed that only a single $^1\pi$ state (state $A \sim \nu = 44\,000$ cm^{-1}) will produce a perturbation of the ground level. The case of pure precession will however yield a perturbation several times the observed value, which is to be expected if an intermediate case applies.

We have no explicit way of quantitatively calculating the perturbation from first principles since the pure precession case only yields an upper limit and the other pure case (united atom) gives a zero result. However if we make use of the data on the isotopic molecule DCl[35] and follow a procedure analogous to that used by Rosenblum et al.[3] for CO we can evaluate the perturbation.

Rosenblum et al.[3] have been able to determine the

total perturbing effect of the upper levels on the B_e of CO by means of determination of both the magnitude and the sign of the magnetic moment of the molecule. Application of Mulliken and Christy's[10] relationship for the case of pure precession to the data for CO gives a result of the same order of magnitude as the integrated effect measured by Rosenblum et al.[3]

We can derive the isotopic behavior of the perturbation from the CO data of Rosenblum et al.[3] Inspection of the measurements of the magnetic moments of the isotopic CO molecules reveals that μ, the magnetic moment, is inversely proportional to the reduced mass. Thus the effect of the magnetic moment to perturb B_e will be $\delta_B{}^i = \rho^4 \delta_B$. The ρ^4 dependence of $\delta_B{}^i$ can also be inferred from Mulliken and Christy's[10] treatment [Eq. (8)] of the Van Vleck case of pure precession.

If we designate the unperturbed value of B_e by B^* and the (observed) perturbed value by B_e then $B_e =$

TABLE VIII. Calculated and observed frequencies in vacuum wave numbers of the 2−0 band of DCl[35].[a]

J	$R(J)$ Calc	$R(J)$ Obs	$\times 10^{-3}$ C−O	Std	$P(J)$ Calc	$P(J)$ Obs	$\times 10^{-3}$ C−O	Std
0	4138.7686	.7646	4.0	C				
1	48.6527	.6516	1.1	B	4117.6490	.6491	−0.1	A
2	58.0819	.0816	0.3	C	06.4201	.4243	−4.2	A
3	67.0531	.0489	4.2	K	4094.7497	.7500	−0.3	A
4	75.5632	.5638	−0.6	B	82.6412	.6440	−2.8	A
5	83.6091	.6090	0.1	C	70.0982	.0973	0.9	A
6	91.1878	.1862	1.6	C	57.1243	.1257	−1.4	A
7	98.2965	.2948	1.7	C	43.7231	.7235	−0.4	A
8	4204.9323	.9342	−1.9	B	29.8983	.8973	1.0	A
9	11.0925	.0942	−1.7	K	15.6537	.6547	−1.0	A
10	16.7742	.7749	−0.7	K	00.9929	.9904	2.5	2−0 HCl
11	21.9750	.9745	0.5	B	3985.9199	.9215	−1.6	A
12	26.6926	.6927	−0.1	B	70.4385	.4396	−1.1	A
13	30.9236	.9208	2.8	B	54.5529			
14	34.6665	.6673	−0.8	K	38.2661			
15					21.5831	.5831	0.0	A

[a] $r_e = 1.28 \times 10^{-3}$.

$B_e^*+\delta_B$. The application of the isotope relations yields

$$\delta_B = B_e(\rho^2 - \rho_D^2)/\rho^2 - \rho^4, \tag{7}$$

where ρ is the value determined from the atomic masses and ρ_D is the value determined from measurement of the perturbed B_e values.

Rosenblum et al.[3] have pointed out that there are three corrections to make to B_e observed before the ratios of the isotopic B_e's are equal to ρ^2.

(1) Correction for upper electronic states.
(2) "Wobble" stretching.
(3) Dunham correction.

These authors have stated the corrections (2) and (3) depend on the same power of ρ and can be made simultaneously in the case of B_e. We have applied Eq. (7) to our data and find $\delta_B = +1.152 \times 10^{-3}$ yielding $B_e^* = 10.592428$ and $B_e^{*i} = 5.448536$.

In the case of B_e we have forced agreement between ρ (as determined by making the Dunham and upper electronic state corrections to the experimental data) and ρ calculated from the atomic masses. The "wobble" stretching correction is (a) either too small to observe or (b) is masked in the determination of δ_{B_e}.

TABLE IX. Molecular constants for DCl³⁵. The dots indicate that the corresponding values were used in the fitting.

	B_v Obs	B_v Calc		Y_{lj} Experimental	Y_{lj} Dunham
B_0	5.392261	...	$Y_{01} \sim B_e$	5.448794₅	(true
B_1	5.279816	5.279819	$Y_{11} \sim \alpha$	−0.1132911	$B_e = 5.4488411$)
B_2	5.168106	...	$Y_{21} \sim \gamma$	$+4.5887 \times 10^{-4a}$	
			$Y_{31} \sim \delta$	-2.1031×10^{-5a}	
	μ_0 Obs	μ_0 Calc			
1−0	2091.0613	...	$Y_{10} \sim \omega_e$	2145.1630	(true
2−0	4128.4330	...	$Y_{20} \sim x_e \omega_e$	−27.18252	$\omega_e = 2145.1973$)
			$Y_{30} \sim y_e \omega_e$	$+0.086493^a$	
			$Y_{40} \sim z_e \omega_e$	-0.003553^a	

a Obtained from HCl³⁵ Y_{lj}'s and isotope relationships.

The experimental observation that ρ_D as determined from ω_e is $\equiv \rho$ as determined from the atomic masses seems to show that the perturbation produced on ω_e by the upper electronic levels is proportional to ω_e or too small to be observed.

The sign of the perturbation on B_e is such that the magnetic moment of the HCl³⁵ molecule must be presumed to be positive, a result not unexpected for hydrides. It can be calculated that the μ_J values for HCl³⁵ and DCl³⁵ are $+0.2$ and $+0.1$ nuclear magnetons, respectively.